

CLAIMS

- [1] A crystal manufacturing apparatus that grows Group III nitride crystals using a crystal raw material solution containing Group III elements, nitrogen and at least one of an alkali metal and an alkaline-earth metal, the
5 Group III nitride crystals being grown in an atmosphere of gas containing nitrogen by applying heat and pressure thereto so as to allow the nitrogen and the Group III elements in the crystal raw material solution to react with each other, the apparatus comprising:
- a reactor vessel in which the crystal raw material solution can be
10 placed; and
- a gas supplying device for introducing the gas containing nitrogen into the reactor vessel,
wherein the reactor vessel and the gas supplying device are coupled,
the reactor vessel has a gas inlet and a gas outlet, and
15 gas containing nitrogen out of the gas containing nitrogen introduced through the gas inlet that is not used for the reaction is exhausted through the gas outlet.
- [2] The apparatus according to claim 1, further comprising:
20 a pressure-resistant vessel; and
a heater that applies heat to the reactor vessel,
wherein the reactor vessel is stored in the pressure-resistant vessel,
and
the reactor vessel and the gas supplying device are coupled via the
25 gas inlet.
- [3] The apparatus according to claim 2,
wherein the gas containing nitrogen supplied from the gas supplying device firstly passes through the gas inlet and is introduced into the reactor
30 vessel, and then can be exhausted through the gas outlet to at least one of an

inside of the pressure-resistant vessel and an outside of the pressure-resistant vessel.

[4] The apparatus according to claim 1, wherein the gas inlet and the gas outlet are formed to be adjacent to each other.

[5] The apparatus according to claim 1, comprising a plurality of gas outlets, wherein the gas outlets are formed adjacent to the perimeter of the gas inlet.

10

[6] The apparatus according to claim 1, further comprising a baffle plate with a through hole formed therein,

wherein the baffle plate is placed in the reactor vessel closer to a liquid surface of the crystal raw material solution than the gas inlet and the gas outlet.

[7] The apparatus according to claim 6, wherein the baffle plate is placed so that the gas inlet and the through hole of the baffle plate are aligned.

20

[8] The apparatus according to claim 7, wherein a cross-sectional shape of the through hole of the baffle plate is a taper shape that widens gradually toward a side of the gas inlet.

[9] The apparatus according to claim 1, further comprising:

25

a cooling tube; and

a gas exhaustion tube,

wherein the gas exhaustion tube is placed at the gas outlet, and

the cooling tube is placed close to or in contact with the perimeter of the gas exhaustion tube.

30

- [10] The apparatus according to claim 9, wherein the gas outlet is formed at a side wall face of the reactor vessel.
- [11] The apparatus according to claim 9, wherein the gas outlet is formed at a top wall face of the reactor vessel.
- [12] The apparatus according to claim 11,
wherein the gas exhaustion tube is placed outside of the reactor vessel via the gas outlet, and
the gas exhaustion tube has a funnel shape.
- [13] The apparatus according to claim 12, further comprising a drops guide,
wherein one end of the drops guide is placed at the gas exhaustion tube, and the other end is placed in the crystal raw material solution or in the vicinity of a liquid surface of the crystal raw material solution, and
an internal structure of the gas exhaustion tube includes funnel structures stacked as a multistage, in which adjacent funnel structures have centers displaced from each other.
- [14] The apparatus according to claim 2,
wherein a junction is placed at the gas inlet or at both of the gas inlet and the gas outlet, and
the reactor vessel is detachable from the inside of the pressure-resistant vessel.
- [15] The apparatus according to claim 14, wherein a gas open/close mechanism is placed at at least one of the gas inlet and the gas outlet.
- [16] The apparatus according to claim 1, wherein the gas inlet and the gas

outlet have inner diameters of 10 mm or less.

[17] The apparatus according to claim 1, wherein an extra length portion is provided to at least one of the gas inlet and the gas outlet.

5

[18] The apparatus according to claim 17, wherein a shape of the extra length portion is like a coil-form or a waveform.

10 [19] The apparatus according to claim 17, wherein a length of the extra length portion is 5 mm or more.

[20] The apparatus according to claim 17, wherein a length of the extra length portion is 20 mm or more.

15 [21] The apparatus according to claim 17, wherein a length of the extra length portion is 100 mm or more.

20 [22] The apparatus according to claim 2, wherein the gas containing nitrogen supplied from the gas supplying device controls ambient pressures of both in the reactor vessel and in the pressure-resistant vessel.

[23] The apparatus according to claim 22, further comprising:
a gas flow rate regulator; and
a pressure regulator,

25 wherein the gas containing nitrogen is introduced from the gas supplying device to the reactor vessel via the gas flow rate regulator,
the pressure-resistant vessel has a gas outlet, to which the pressure regulator is connected, and
the gas flow rate regulator and the pressure regulator allow ambient pressures in the reactor vessel and in the pressure-resistant vessel to be

30

controlled.

[24] The apparatus according to claim 23, further comprising a recovery device,

5 wherein the recovery device is connected to the pressure regulator, and

the recovery device allows recovery of at least one of the alkali metal and the alkaline-earth metal evaporating from the crystal raw material solution.

10

[25] The apparatus according to claim 2,

wherein the gas supplying device comprises a first gas supplying device and a second gas supplying device,

the pressure-resistant vessel has a gas inlet,

15

the first gas supplying device is connected to the gas inlet of the reactor vessel,

the gas outlet of the reactor vessel directly communicates with an outside of the pressure-resistant vessel,

20

the second gas supplying device is connected to the gas inlet of the pressure-resistant vessel, and

the first gas supplying device and the second gas supplying device allow ambient pressures in the reactor vessel and in the pressure-resistant vessel to be controlled independently.

25

[26] The apparatus according to claim 25, wherein the pressure-resistant vessel further has a gas outlet.

[27] The apparatus according to claim 26, further comprising:

a first gas flow rate regulator;

30

a second gas flow rate regulator;

- a first pressure regulator; and
a second pressure regulator,
wherein gas containing nitrogen is introduced from the first gas supplying device to the reactor vessel via the first gas flow rate regulator,
- 5 the gas outlet of the reactor vessel is connected to the first pressure regulator,
gas is introduced from the second gas supplying device to the pressure-resistant vessel via the second gas flow rate regulator,
the gas outlet of the pressure-resistant vessel is connected to the
- 10 second pressure regulator,
the first gas flow rate regulator and the first pressure regulator allow an ambient pressure in the reactor vessel to be controlled, and
the second gas flow rate regulator and the second pressure regulator allow an ambient pressure in the pressure-resistant vessel to be controlled.
- 15
- [28] The apparatus according to claim 1, wherein a flow velocity of the gas containing nitrogen at at least one of the gas inlet and the gas outlet of the reactor vessel is 1 cm/sec to 500 cm/sec.
- 20 [29] The apparatus according to claim 27, wherein the gas containing nitrogen introduced to the reactor vessel and the gas introduced to the pressure-resistant vessel have different purities.
- 25
- [30] The apparatus according to claim 29, wherein a purity of the gas containing nitrogen introduced to the reactor vessel is 99.9% or more and a purity of the gas introduced to the pressure-resistant vessel is 99% or less.
- 30
- [31] The apparatus according to claim 27, wherein the gas containing nitrogen introduced to the reactor vessel and the gas introduced to the pressure-resistant vessel are different in types.

- [32] The apparatus according to claim 31, wherein the gas containing nitrogen introduced to the reactor vessel is nitrogen, and the gas introduced to the pressure-resistant vessel is a rare gas.
- 5 [33] The apparatus according to claim 31, wherein the gas containing nitrogen introduced to the reactor vessel is nitrogen, and the gas introduced to the pressure-resistant vessel is air.
- 10 [34] The apparatus according to claim 27, further comprising a recovery device,
wherein the recovery device is connected to the first pressure regulator, and
the recovery device allows recovery of at least one of the alkali metal and the alkaline-earth metal evaporating from the crystal raw material
15 solution.
- [35] The apparatus according to claim 2, wherein the heater is an induction heating type heater.
- 20 [36] The apparatus according to claim 1,
wherein the Group III elements are at least one selected from the group consisting of gallium, aluminum and indium, and
the crystals are $\text{Al}_x\text{Ga}_y\text{In}_{1-x-y}\text{N}$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq x+y \leq 1$.
- 25 [37] The apparatus according to claim 1, wherein the gas containing nitrogen is a nitrogen gas, an ammonia gas or a mixed gas of the nitrogen gas and the ammonia gas.
- 30 [38] The apparatus according to claim 37, wherein the gas containing nitrogen further comprises at least one of an inert gas and hydrogen gas.

- [39] A crystal manufacturing method, comprising the steps of:
- 5 preparing a crystal raw material solution containing Group III elements, nitrogen and at least one of an alkali metal and an alkaline-earth metal in a reactor vessel,
- 10 applying heat and pressure thereto in an atmosphere of gas containing nitrogen so as to allow the nitrogen and the Group III elements in the crystal raw material solution to react with each other, whereby Group III nitride crystals are grown,
- 15 wherein the reactor vessel has a gas inlet and a gas outlet, the reactor vessel and a gas supplying device are coupled, and in the reactor vessel, gas containing nitrogen out of gas containing nitrogen introduced through the gas inlet that is not used for the reaction is exhausted through the gas outlet.
- 20 [40] The manufacturing method according to claim 39, wherein the reactor vessel is stored in a pressure-resistant vessel, the reactor vessel and the gas supplying device are coupled via the gas inlet, and
- gas containing nitrogen supplied from the gas supplying device firstly is introduced to the reactor vessel through the gas inlet, and then is exhausted through the gas outlet to at least one of an inside of the pressure-resistant vessel and an outside of the pressure-resistant vessel.
- 25 [41] The manufacturing method according to claim 39, wherein, in the reactor vessel, a concentration gradient is formed for at least one of the alkali metal and the alkaline-earth metal evaporating from the crystal raw material solution.
- 30 [42] The manufacturing method according to claim 39, wherein a flow

velocity of the gas containing nitrogen at at least one of the gas inlet and the gas outlet of the reactor vessel is regulated at 1 cm/sec to 500 cm/sec.

[43] The manufacturing method according to claim 40, wherein a junction
5 is placed at the gas inlet or at both of the gas inlet and the gas outlet, and
the reactor vessel is detachable from the inside of the
pressure-resistant vessel.

[44] The manufacturing method according to claim 43,
10 wherein a gas open/close mechanism is placed at at least one of the
gas inlet and the gas outlet,
prior to crystal manufacturing, outside of the pressure-resistant
vessel, putting a crystal raw material containing Group III elements and at
least one of an alkaline-earth metal and an alkaline-earth metal in the
15 reactor vessel in an atmosphere of an inert gas,
closing the gas open/close mechanism and hermetically sealing the
reactor vessel,
storing the reactor vessel in the pressure-resistant vessel,
connecting with the gas supplying device via the junction,
20 opening the gas open/close mechanisms, and
in this state, allowing the gas to be introduced to the reactor vessel.

[45] The manufacturing method according to claim 44, further comprising
the step of, after putting the crystal raw material in the reactor vessel in an
25 atmosphere of an inert gas outside of the pressure-resistant vessel, heating
the reactor vessel to form the crystal raw material solution.

[46] The manufacturing method according to claim 45, further comprising
the step of, after forming the crystal raw material solution by heating the
30 reactor vessel, performing agitation of the crystal raw material solution.

[47] The manufacturing method according to claim 40,
wherein gas containing nitrogen is introduced from the gas supplying
device to the reactor vessel via a gas flow rate regulator,

5 the pressure-resistant vessel has a gas outlet, to which a pressure
regulator is connected,

the gas flow rate regulator and the pressure regulator allow ambient
pressures in the reactor vessel and in the pressure-resistant vessel to be
controlled, and

10 the gas containing nitrogen introduced to the reactor vessel is the
same as gas introduced into the pressure-resistant vessel.

[48] The manufacturing method according to claim 40,
wherein the pressure-resistant vessel has a gas inlet,

15 a first gas supplying device is connected to the gas inlet of the reactor
vessel,

the gas outlet of the reactor vessel directly communicates with an
outside of the pressure-resistant vessel,

20 a second gas supplying device is connected to the gas inlet of the
pressure-resistant vessel,

the first gas supplying device and the second gas supplying device
allow ambient pressures in the reactor vessel and in the pressure-resistant
vessel to be controlled independently, and

25 the gas containing nitrogen introduced to the reactor vessel is
different from gas introduced into the pressure-resistant vessel.

[49] The manufacturing method according to claim 48, wherein the gas
containing nitrogen introduced to the reactor vessel is nitrogen, and the gas
introduced to the pressure-resistant vessel is a rare gas.

- [50] The manufacturing method according to claim 48, wherein the gas containing nitrogen introduced to the reactor vessel is nitrogen, and the gas introduced to the pressure-resistant vessel is air.
- 5 [51] The manufacturing method according to claim 48, wherein the pressure-resistant vessel further has a gas outlet.
- [52] The manufacturing method according to claim 51,
wherein gas containing nitrogen is introduced from the first gas
10 supplying device to the reactor vessel via a first gas flow rate regulator,
the gas outlet of the reactor vessel is connected to a first pressure
regulator,
gas is introduced from the second gas supplying device to the
pressure-resistant vessel via a second gas flow rate regulator,
15 the gas outlet of the pressure-resistant vessel is connected to a second
pressure regulator,
the first gas flow rate regulator and the first pressure regulator allow
an ambient pressure in the reactor vessel to be controlled, and
the second gas flow rate regulator and the second pressure regulator
20 allow an ambient pressure in the pressure-resistant vessel to be controlled.
- [53] The manufacturing method according to claim 40,
wherein the pressure-resistant vessel has a gas inlet,
a first gas supplying device is connected to the gas inlet of the reactor
25 vessel,
the gas outlet of the reactor vessel directly communicates with an
outside of the pressure-resistant vessel,
a second gas supplying device is connected to the gas inlet of the
pressure-resistant vessel,
30 the first gas supplying device and the second gas supplying device

allow ambient pressures in the reactor vessel and in the pressure-resistant vessel to be controlled independently, and

the gas containing nitrogen introduced to the reactor vessel and gas introduced into the pressure-resistant vessel have different purities.

5

[54] The manufacturing method according to claim 53, wherein a purity of the gas containing nitrogen introduced to the reactor vessel is 99.9% or more and a purity of the gas introduced to the pressure-resistant vessel is 99% or less.

10

[55] The manufacturing method according to claim 53, wherein the pressure-resistant vessel further has a gas outlet.

[56] The manufacturing method according to claim 55,

15 wherein gas containing nitrogen is introduced from the first gas supplying device to the reactor vessel via a first gas flow rate regulator, the gas outlet of the reactor vessel is connected to a first pressure regulator,

gas is introduced from the second gas supplying device to the 20 pressure-resistant vessel via a second gas flow rate regulator,

the gas outlet of the pressure-resistant vessel is connected to a second pressure regulator,

the first gas flow rate regulator and the first pressure regulator allow an ambient pressure in the reactor vessel to be controlled, and

25 the second gas flow rate regulator and the second pressure regulator allow an ambient pressure in the pressure-resistant vessel to be controlled.

[57] The manufacturing method according to claim 40, wherein prior to crystal manufacturing, an impurity gas removal treatment is performed for

30 at least one of the reactor vessel and the pressure-resistant vessel.

- [58] The manufacturing method according to claim 57, wherein the impurity gas removal treatment is at least one of baking and evacuation.
- 5 [59] The manufacturing method according to claim 39, wherein the Group III elements are at least one selected from the group consisting of gallium, aluminum and indium, and the crystals are $\text{Al}_x\text{Ga}_y\text{In}_{1-x-y}\text{N}$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq x+y \leq 1$.
- 10 [60] The manufacturing method according to claim 39, wherein the gas containing nitrogen is a nitrogen gas, an ammonia gas or a mixed gas of the nitrogen gas and the ammonia gas.
- 15 [61] The manufacturing method according to claim 60, wherein the gas containing nitrogen further comprises at least one of an inert gas and hydrogen gas.
- [62] A semiconductor element comprising Group III nitride crystals manufactured by the manufacturing method according to claim 39.
- 20 [63] A semiconductor light-emitting device comprising Group III nitride crystals manufactured by the manufacturing method according to claim 39.